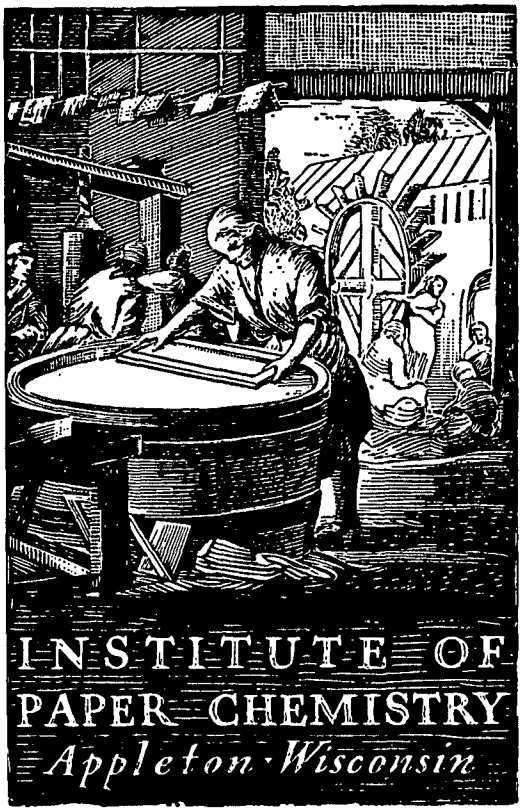

OXIDATIVE DELIGNIFICATION WITH OXYGEN/ALKALI TO HIGH-YIELD PULPS

PULPING OF HARDWOODS – RED MAPLE

Project 3264

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 17, 1977

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Oxygen/alkali pulping of a typical hardwood (red maple) for high-yield (64-72%) pulps was carried out at both high and low consistency. Most of the work was done on fiberized chips to improve the homogeneity and rate of reaction with oxygen. The effect of cooking parameters on yield was determined, and strength properties were obtained. In general, the strength properties were somewhat lower than the reference kraft pulp (50% yield) and holopulp (71% yield). The oxygen pulps gave higher yields, higher unbleached brightnesses, and beat faster than the reference kraft pulp. Low consistency gave higher brightness and viscosity than high consistency oxygen pulping. In addition, low consistency was found to offer potential for pulping whole hardwood chips, rather than requiring fiberized chips. Two of the pulps were bleached to ca. 85 brightness, at which point they still gave a yield advantage over kraft (54-58 vs. 47%). Future work will concentrate on a similar approach to pulping loblolly pine.

OBJECTIVE

The main objective of this project is to study the effect of pulping parameters on oxygen/alkali delignification for preparing high-yield papermaking pulps from softwoods and hardwoods. The goal is to provide papermaking pulps with unbleached yields greater than 65% and bleached pulps of 55% or greater yield coupled with TAPPI brightnesses ranging up to at least 85.

INTRODUCTION

The kraft process is capable of producing a wide range of pulps from a variety of fiber sources. Therefore, it has found wide acceptance in the pulp and paper industry. The pulps have outstanding strength properties and acceptable bleachability. However, the process suffers from a lack of selectivity in delignification (low yields), a capital intensive chemical recovery system which includes an explosion hazard, and an odor problem which has become more of a liability in recent years due to environmental concern.

Oxidative delignification in general, and oxygen/alkali delignification in particular, offers some distinct advantages over kraft. Odor problems are largely eliminated by removal of sulfur from the cooking chemicals. Less carbohydrate removal leads to more selective delignification. Finally, the possibility of using sodium carbonate and/or sodium bicarbonate provides the prospect of a simplified chemical recovery system which does not require the causticizing sequence of the standard kraft system. Also, a recovery system based on wet air oxidation (wet combustion) may be a viable alternative.

Much of the work reported in the literature has been done at fairly low yield levels. The results published by the Empire State Paper Research Institute, which has emphasized softwoods, has concentrated on the 45-50% yield level (1). North Carolina State has worked in the 44-56% yield range on southern pine (2). The Forest Products Laboratory has done some work at the higher yield level (up to 65%), but this has all been on softwoods (3). Samuelson and coworkers have probably done the most in the high yield range (up to 70%), and have worked on both softwood and hardwood, but very little strength data are given (4). The Pulp and Paper Research Institute of Canada has concentrated on spruce, with

strength data being given mainly in the 45-58% yield range (5). The Japan Pulp and Paper Research Institute reported work on beech in the 50-55% yield range (6).

The present project is intended to prepare high-yield (ca. 65-70%) pulps, using sodium carbonate or a mixture of sodium carbonate and bicarbonate as alkali. The experimental approach is guided by earlier experience at the Institute (7) on oxidative delignification using the very selective oxidant, chlorine dioxide (holopulping). Thus, the following steps were incorporated into the initial study:

chip pretreatment, including chip fiberization
oxygen/alkali delignification (pulping sequence)
disc refining, if necessary
further delignification (bleaching sequence)

This is shown in schematic form in Fig. 1.

The chip fiberization was felt to be necessary because of the well-known lack of penetration in oxygen/alkali (OA) pulping (5c,8), which is consistent with earlier experience with chlorine dioxide (7). It was carried out under conditions which were designed to minimize fiber damage (see below) but still provide an open material that is readily penetrated by the cooking liquor. The final delignification was envisioned as a more selective process which might not involve oxygen, but might resemble conventional bleaching.

This report contains the results obtained to date on a typical hardwood (red maple). The emphasis has been on unbleached pulps, but a limited amount of data are also included on bleached pulp.

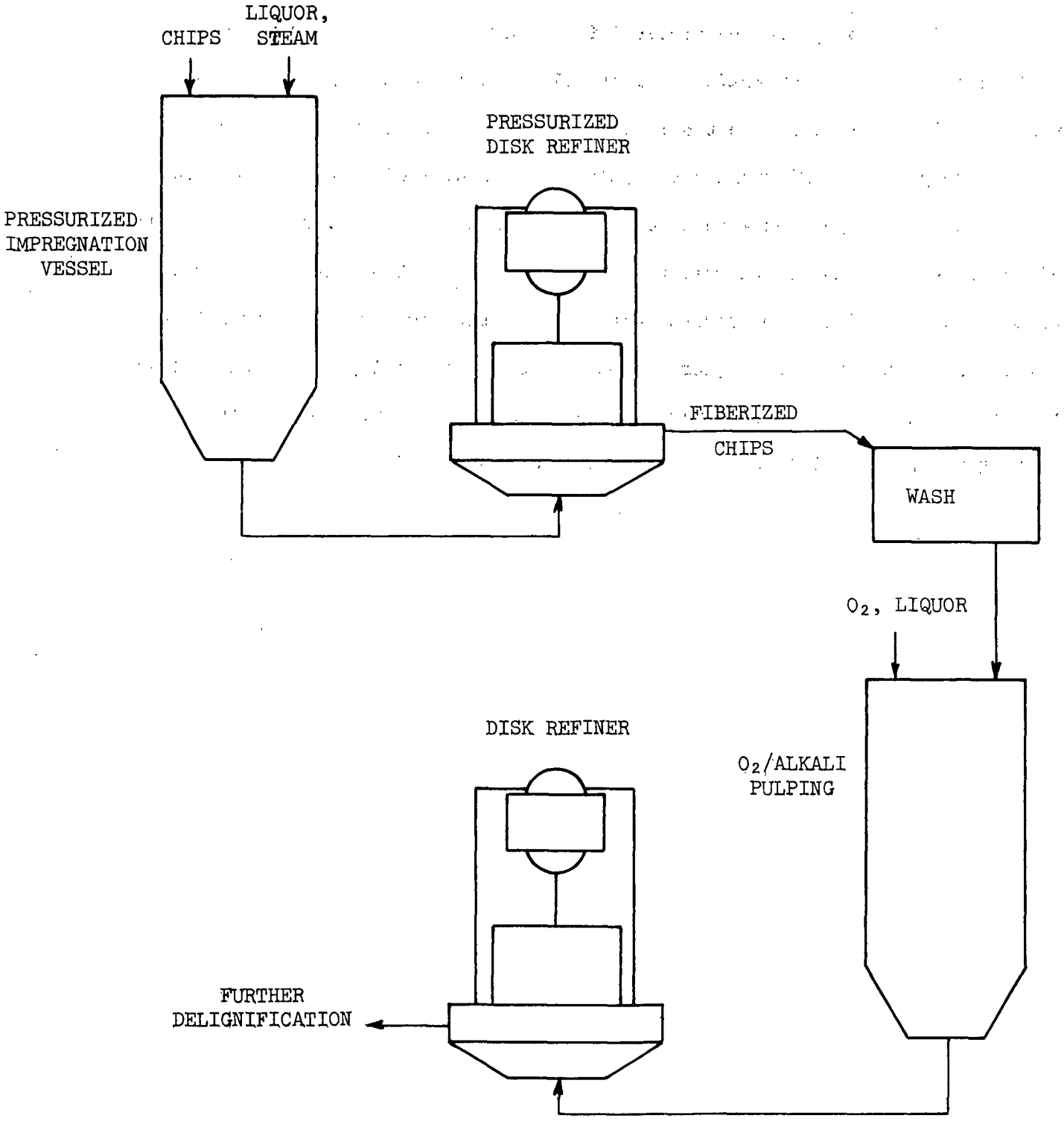

Figure 1. Schematic Representation of Laboratory Sequence for Oxygen/Alkali Pulping

CONCLUSIONS

Oxygen pulps can be prepared from red maple with higher yield and somewhat lower strength than kraft. For example, a 65% yield oxygen pulp can be prepared with 79-100% of the tensile, 55-92% of the tear, and 71-104% of the burst strength of a 50% yield kraft pulp. Potassium iodide has a beneficial effect on pulp properties when used at high consistency, particularly at lower yield and kappa numbers. Magnesium ion has no effect when pulping with sodium carbonate, or a mixture of sodium carbonate and bicarbonate. Low consistency offers higher brightness, higher viscosity, and faster delignification. It is possible to bleach these high-yield oxygen pulps with conventional methods to 85 brightness and still have a yield advantage over kraft.

RESULTS AND DISCUSSION

CHIP FIBERIZATION (PRETREATMENT)

Previous experience (7) had shown that less mechanical damage to fibers occurs when fiberization is carried out at higher temperatures. Thus, fiberization at 160°C was shown to result in less mechanical damage than at 130°C (9). Bauer-McNett classification and strength-property data on pulps, when compared with analogous pulps prepared from pin chips by chlorite treatment, showed that some fiber damage was suffered, but that this damage was acceptable for many papermaking purposes. This is particularly true for short fiber, hardwood pulps, which are not used primarily for strength.

A further advantage of fiberization at 160° is that by working above the glass transition point of lignin, the chips tend to separate at the middle lamella, leaving a lignin-rich surface for selective delignification. This is the opposite of what is desired for producing thermomechanical pulp, where a cellulose-rich surface is desired for optimal bonding. The latter is favored by fiberization at lower temperature.

Two different processes were used in the fiberization. In the first process (RM 75), the wood chips were soaked to 43.4% solids, preheated with 80 psig steam (162°C) for 4.0 min, and fiberized at the same pressure in a Bauer 418 double disc refiner with a plate setting of 0.030 inch. The material from this process was then extracted with 5% sodium hydroxide at 90°C to remove readily soluble materials which increase chemical consumption in oxidative delignification (10). The overall yield for this process was 90%.

The second process (RM 76) involved an impregnation with excess sodium carbonate at 92°C for 30 min at 10% consistency. Excess liquor was drained from the chips leaving 4.9% sodium carbonate on the chips (as Na_2O). This mixture was then heated and fiberized as before at 40% consistency, giving an overall yield of 90% also. Due to technical difficulties in use of the pilot plant equipment, there is an uncertainty of about ±2% in this overall yield figure, but it is consistent with earlier laboratory studies (10).

The first sample (RM 75), after the extraction with sodium hydroxide, appeared to be equivalent to the second sample (RM 76) with respect to its pulping properties, giving similar yields, kappa numbers, and strength properties for similar cooking conditions. This is illustrated in Table I. The second process is simpler, and both might aid in tall oil recovery from softwoods, where it appears that removal with alkali before cooking with oxygen is beneficial (11).

Power consumption data on such small (75 lb) samples are notoriously inaccurate. Nevertheless, the data, given in Table II, illustrate two points: The amount of power input is small, relative to conventional thermomechanical pulping; and power input is probably less in the presence of alkali.

CONDITIONS FOR OA DELIGNIFICATION

Most of the work described in this report was carried out at high consistency (ca. 30%). A 2000 ml stainless steel vessel was equipped with a thermocouple well, inlet for steam and oxygen, and outlet, as shown in Fig. 2. A Teflon basket was used to hold the impregnated, fiberized sample, and contact with the stainless steel was eliminated, since there was no free liquor.

TABLE I

COMPARISON OF PULPS PREPARED FROM RED MAPLE FIBERIZED WITH AND WITHOUT ALKALI

Pulp	42C	118C
Na_2CO_3 in fiberization, % as Na_2O	0	4.9
NaOH extraction	yes	no
Yield after pulping	65.1	63.8[a]
Kappa number	73	60
Klason lignin, %	8.3	7.1
Acid-soluble lignin, %	4.2	4.5
Viscosity, cp	6.6	6.7
Canadian freeness, ml[b]	400	380
Standard drainage, d_s, sec	5.9	5.0
Handsheet density, g/cc	0.66	0.66
Zero-span breaking length, km	12.0	11.1
Burst factor	33	31
Breaking length, km	6.4	5.8
Stretch, %	2.0	2.5

[a]Assuming 90% yield for fiberization.

[b]Drainage and handsheet properties after 100 PFI mill counter revolutions.

TABLE II

POWER CONSUMPTION FOR FIBERIZATION OF RED MAPLE

Sample	Alkali During Fiberization	Power Consumption
RM 75	0	3.9 BHPD/ADT[a]
RM 76	4.9[b]	1.7 BHPD/ADT

[a]Brake horsepower days per air-dry ton.

[b]Sodium carbonate, expressed as sodium oxide.

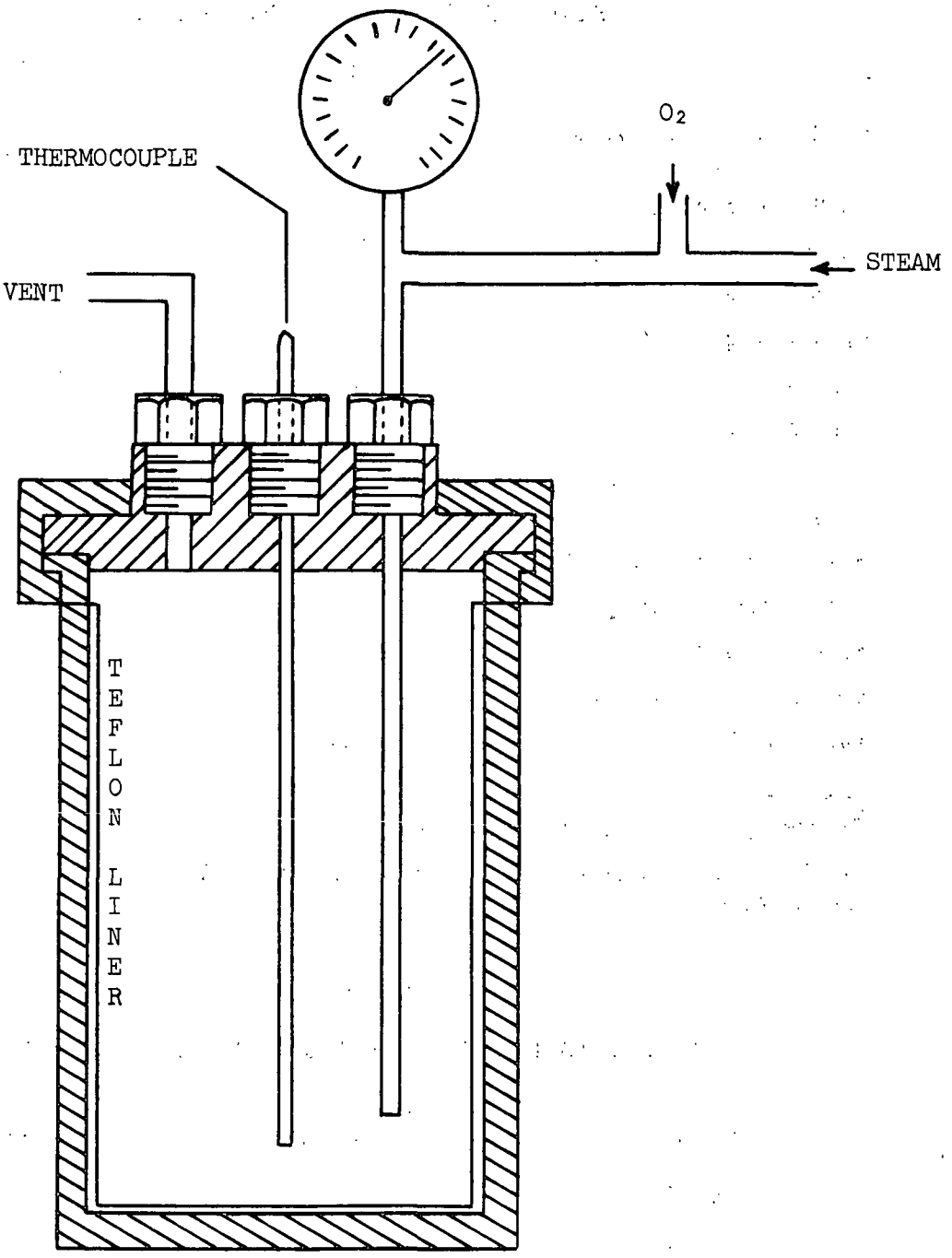

Figure 2. High Consistency Reaction Vessel

Several cooks were also carried out at low consistency, in a system shown in Fig. 3. This system uses air as the oxygen source, at pressures up to 3000 psi. Circulating liquor is heated in the heat exchanger, and sprayed through the shower to facilitate dissolution of air. The liquor then percolates through the sample, effecting delignification. Such conditions give a relatively large excess of cooking liquor and are identified as low consistency pulping. Equivalent terminology would be high liquor-wood ratio for low consistency pulping and low liquor-wood ratio for high consistency pulping.

EFFECT OF PULPING VARIABLES ON YIELD

Effect of Temperature on Yield at High Consistency

Figure 4 shows the yield as a function of time for several temperatures. As expected, the higher the temperature the faster the rate of yield loss. Also shown in the figure are the lignin-free yields (total yield minus total lignin content on an o.d. wood basis) for the same samples. These data are also shown in a three-dimensional form in Fig. 5. Here the upper surface represents total yield, and the lower surface is the carbohydrate (lignin-free) yield. The vertical distance between the surfaces represents lignin content of the pulps, on an o.d. wood basis.

It can be seen that after the initial, rapid yield loss, the slope for total yield is only slightly more negative than for carbohydrate yield, indicating a lack of selectivity. Ideally, the carbohydrate yield would remain constant at a high value. In that respect, the data shown in these figures are somewhat misleading because they are at fairly high yields. The selectivity improves as the yield goes down. A more complete set of data, including samples in the lower yield range, has been analyzed in the appendix by multiple linear regression. In this case better selectivity was found.

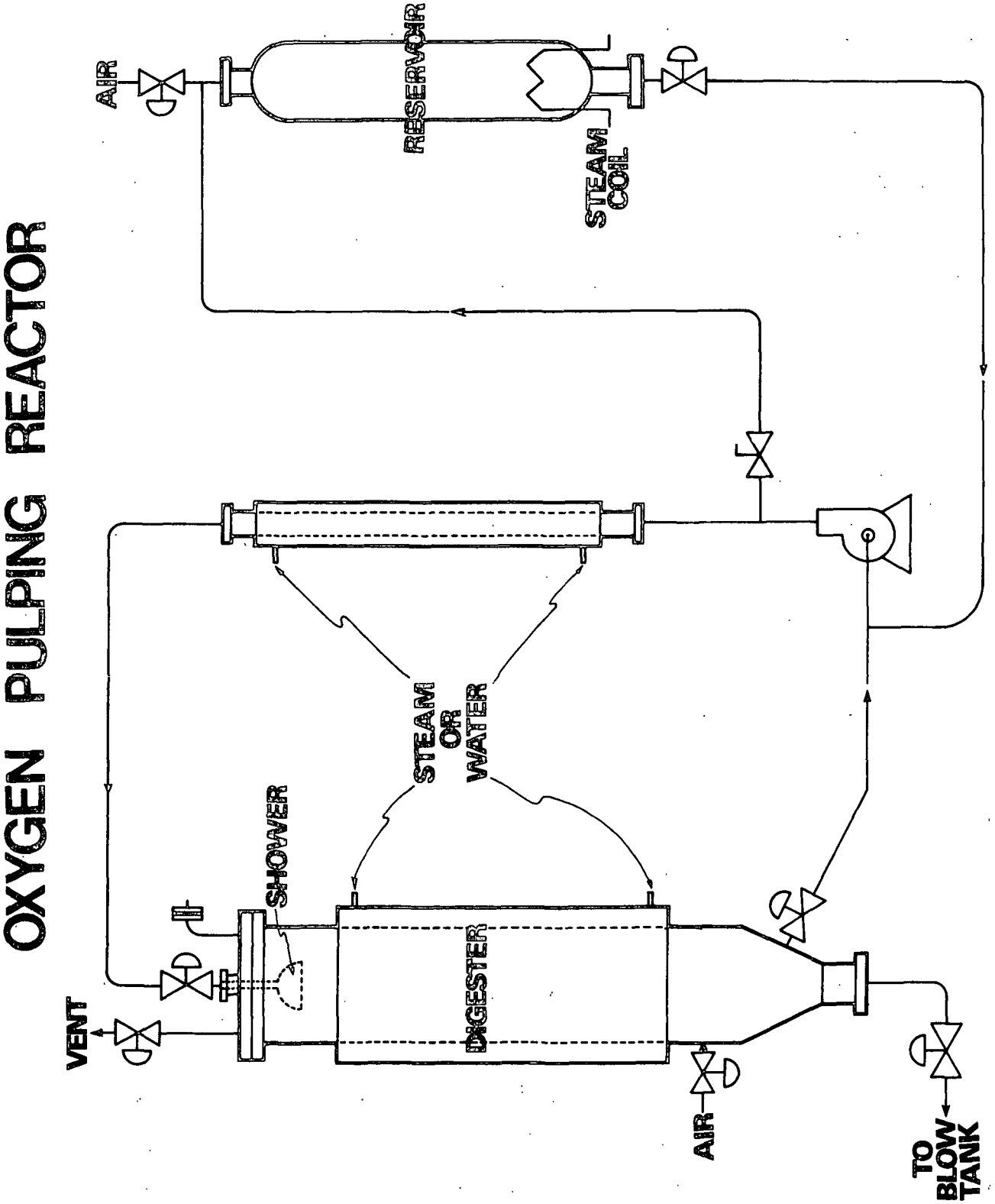

Figure 3. Low Consistency Reactor

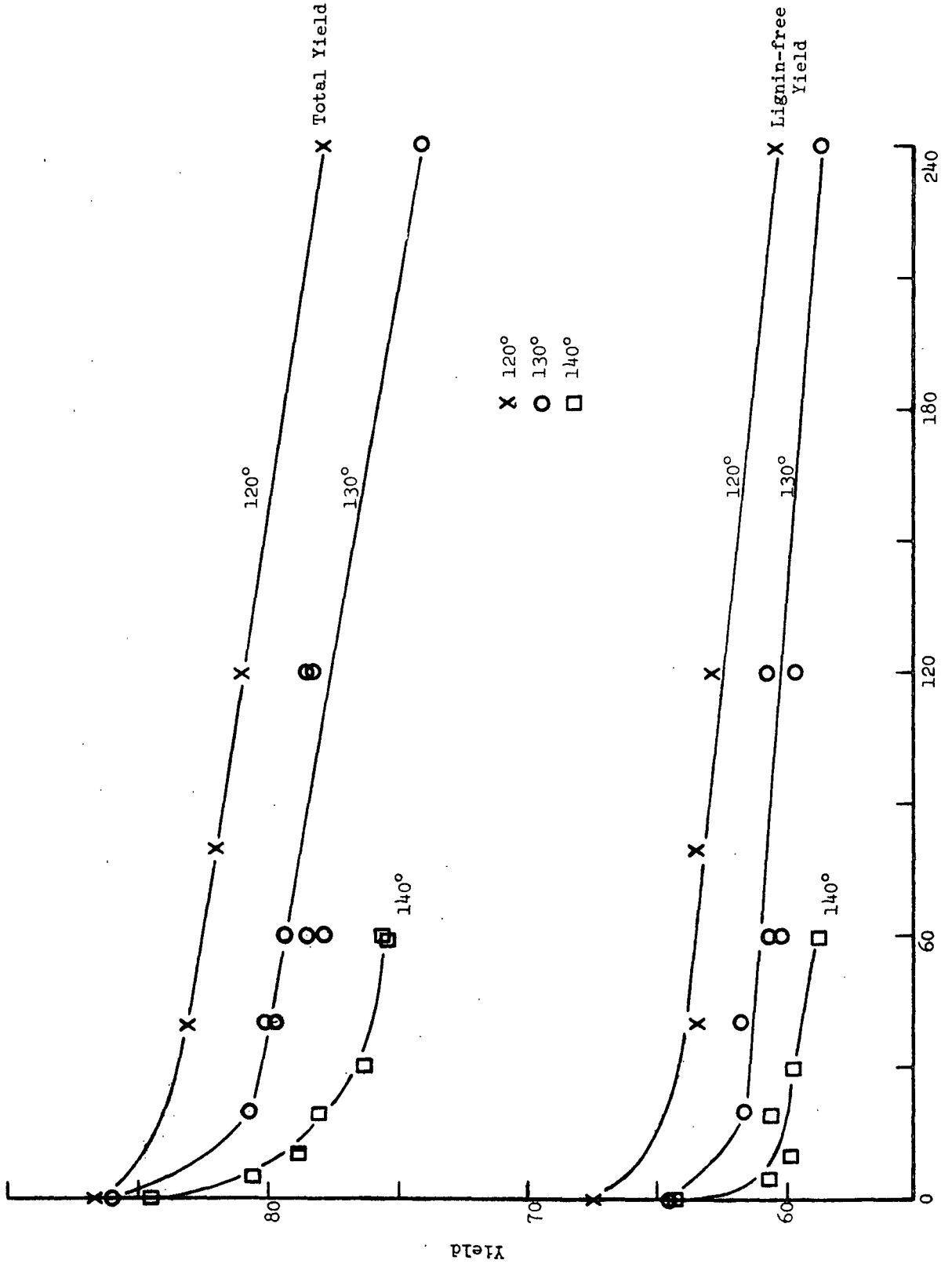

Figure 4. Total Yield and Lignin-free Yield as Functions of Time at Selected Temperatures (130 psi oxygen equivalent)

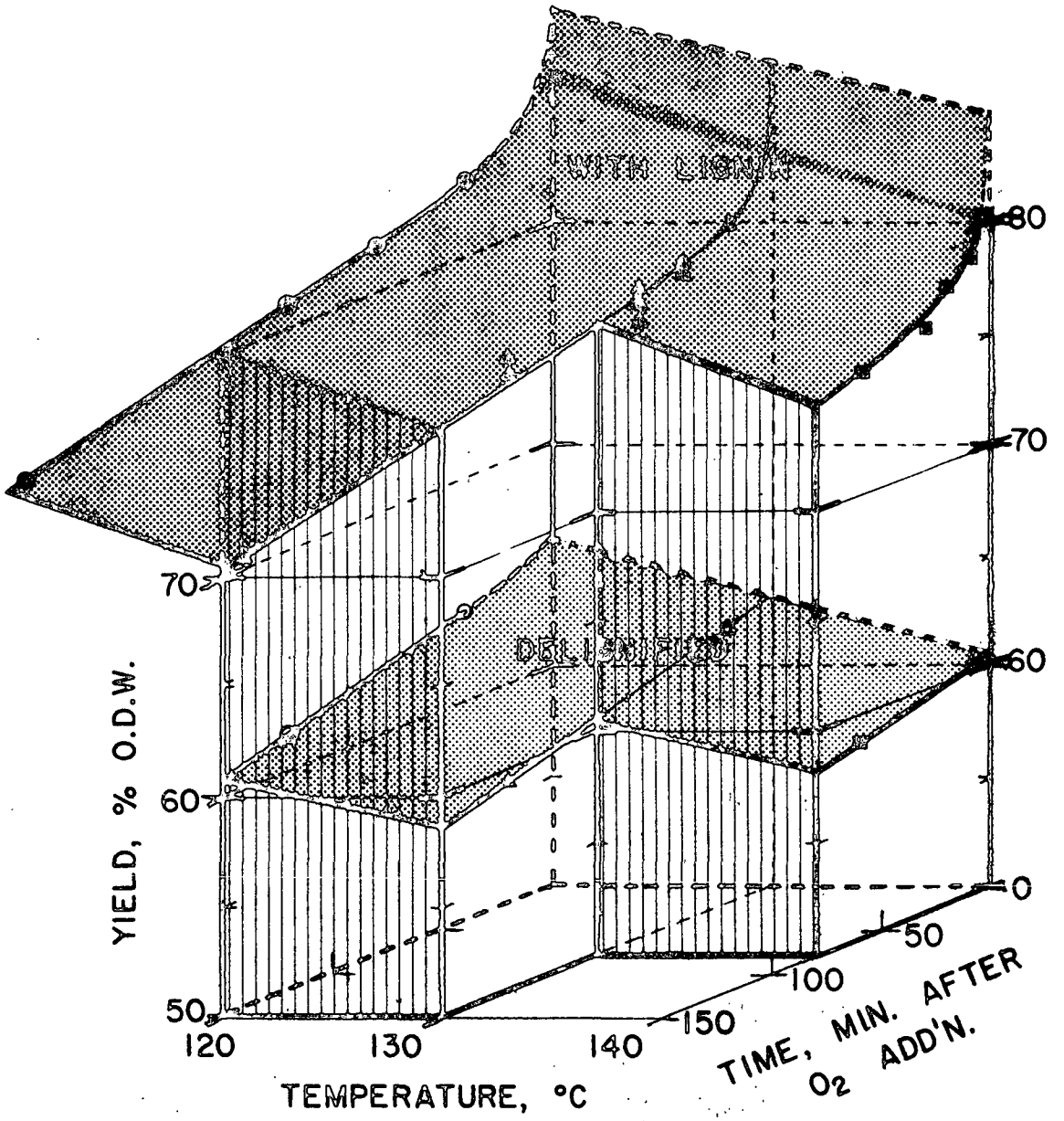

Figure 5. Three-dimensional Representation of Total Yield and Lignin-free Yield as Functions of Time and Temperature (130 psi oxygen equivalent). Same Data as Fig. 4

Effect of Pressure on Yield at High Consistency

A limited number of cooks was carried out at pressures higher and lower than the standard pressure (130 psig at 100°). Table III gives the yield for selected values of temperature, pressure, and time for the sake of comparison. It can be seen that the changes in pressure did not cause a large change in the yield, although lower yields were always observed at higher pressures. These small changes in yield, however, are the equivalent of shortening the reaction times significantly. For example, at 120°, 300 psi for 120 min gave the same yield as 60 psi for 240 min. This indicates transport of oxygen to the reaction site is a factor in the overall reaction kinetics, even at 300 psig oxygen, and that higher availability of oxygen should further increase reaction rates. This was found to be the case when, as will be discussed later, low consistency pulping was employed.

Effect of Potassium Iodide and Magnesium Ion

Potassium iodide has been shown previously (12) to have a stabilizing effect on carbohydrates during oxygen/alkali delignification, presumably through scavenging the peroxides. Magnesium ion has also been shown to have a beneficial effect in oxygen/sodium hydroxide pulping (13), although not in oxygen pulping under mildly alkaline conditions (3a). Therefore, it was of interest to assess the effectiveness of these additives in the present systems. Table IV gives the results of several runs with and without potassium iodide and magnesium ion. The beneficial effect of potassium iodide becomes most impressive when the kappa numbers, lignin contents, and viscosities are considered together, all of which are improved by potassium iodide at high consistency. The higher viscosity with potassium iodide is consistent with carbohydrate stabilization. The lower lignin content and kappa number suggest an increased rate of lignin removal as well. On the other hand, magnesium carbonate had very little effect on these pulp properties. This suggests that peroxide stabilization is not a factor at lower pH.

TABLE III

YIELDS FOR RED MAPLE PULPS AT VARIOUS TEMPERATURES AND PRESSURES

Sample	Temperature, °C	Pressure Equivalent,[a] psi	Time, min	Yield, %
99	120	60	120	81.7
81	120	130	120	81.0
104	120	300	120	79.5
95	120	60	240	79.6
87	120	130	240	78.0
107	120	300	240	76.7
106	130	60	60	79.4
85	130	130	60	78.6
96	130	300	60	77.4
100	130	60	240	76.6
93	130	130	240	74.2

[a] Oxygen concentration equivalent to given pressure at 100°C (corrected for water vapor pressure and ideal gas law).

At low consistency, results were obtained at two different temperatures. The first set of runs (35-38) was done at 120°. Magnesium acetate had little, if any, beneficial effect under those conditions. The second set of runs (130-133) was done at 130° with correspondingly shorter times. Similar yields were obtained and, at 130° at least, potassium iodide had very little effect. This lack of effect in going to low consistency is probably due to dilution of the potassium iodide by the 30-fold increase in the amount of liquor (i.e., a concentration effect).

Effect of Pulping Consistency

Comparing low consistency with high consistency, it can be noted that higher viscosities were generally obtained at low consistency unless potassium iodide was included. Furthermore, shorter reaction times (see footnotes, Table

IV) and higher unbleached pulp brightnesses (see Table X) were also obtained at low consistency. One additional advantage of low consistency, which might be more important in industrial-scale pulping, is that the greater amount of liquor makes it easier to control the exothermic reaction which is observed at high consistency.

TABLE IV

EFFECT OF POTASSIUM IODIDE AND MAGNESIUM CARBONATE ON PULP YIELD AND PROPERTIES

Sample	Additive[a]	Yield,[b] %	Viscosity,[c] cp	Kappa[c]	Lignin,[c,d] %
High consistency[e]					
30B, 39B, 40B	None	65.5	6.5	78	12.7
62B, 63B, 64B, 65B	1% $MgCO_3$	64.4	7.2	66	11.5
66B, 67B, 68B, 69B	10% KI	66.0	15.6	51	9.4
Low consistency					
35, 38[f]	None	69.7	11.1	89[b]	15.6
36[g]	None	66.4	9.9	73	13.3
37[f]	5% $Mg(OAc)_2$	68.7	12.7	88	14.9
130[h]	None	66.8	9.7	79	14.1
131[h]	10% KI	67.2	10.5	79	14.1
132[h]	10% KI	65.5	9.2	80	15.0
133[h]	None	63.6	7.5	73	14.6

[a] o.d. wood basis.

[b] Average for samples listed.

[c] Measured on composite of listed samples, unless otherwise indicated.

[d] Sum of Klason and acid-soluble lignin.

[e] Pulping conditions: 120°, 640 min total at temp., 10.5% Na_2CO_3 (as Na_2O).

[f] Pulping conditions: 120°, 165 min total at temp.

[g] Pulping conditions: 120°, 210 min total at temp.

[h] Pulping conditions: 130°, 90 min total at temp.

The reasons for these advantages at low consistency are not yet clear. The circulation of the liquor, the liquor-to-wood ratio, the alkali-to-wood ratio, and the pressure (and reaction gas, i.e.. air vs. oxygen) are all changed in going from one system to the other. These factors will be the subject of further work.

STRENGTH PROPERTIES OF UNBLEACHED PULPS

Effect of Yield on Sheet Properties

Table V gives selected sheet properties for high consistency oxygen pulps at three different yield levels, ranging from 80 to 65. The data are interpolated values from PFI mill runs at different refining intervals, so that the comparison can be made at the same sheet density. When the comparison is made on this basis, tear and freeness are the only two properties which changed appreciably with yield. However, continuing the refining of the lower yield pulp resulted in sheets of greater density, which showed better strength properties. Continuing the refining of the high-yield pulp trying to get denser sheets would give freeness values which would be unacceptably low for most uses.

TABLE V

INFLUENCE OF YIELD ON SHEET PROPERTIES AT CONSTANT SHEET DENSITY FOR UNBLEACHED HIGH CONSISTENCY OXYGEN/ALKALI PULPS

Sample	11C	19C	39C
Yield, % (kappa number)	80(128)	72(100)	65(72)
PFI mill, counter rev's	550	75	0
Canadian freeness, ml	270	480	550
Handsheet density, g/cc	0.60	0.60	0.60
Zero-span breaking length, km	12.3	12.0	11.8
Burst factor	24	25	25
Breaking length, km	5.3	5.2	5.3
Tear factor (Elmendorf)	38	42	47

Interestingly, the zero-span breaking length did not change appreciably, even though there would be almost 20% more fibers in the lowest yield handsheets. If anything, the trend appears to be in the opposite direction. Also to be noted is the difference in refining characteristics. The highest yield pulp required much longer in the PFI mill than the other two to obtain the 0.6 density. In fact, the lowest yield pulp gave that sheet density even without refining. This suggests

a trend which is observed with oxygen/alkali pulps in general: at lower yield levels, they tend to be very fast beating.

Comparison of Strength Properties with Other Pulps

In order to evaluate the pulps, comparisons were made with kraft and chlorine dioxide-alkali pulps made from red maple. The kraft pulp was made at the 50% yield level, and was chosen to represent a typical commercial pulp. The chlorine dioxide-alkali pulp (holopulp) was chosen to represent the potential of a very selective, oxidative pulp. It was prepared at a yield and kappa number similar to the oxygen pulps, and the results are given in Table VI.

TABLE VI

TEST DATA FOR UNBLEACHED KRAFT AND HIGH YIELD OXIDATIVE PULPS AT TWO SHEET DENSITIES

Sample	19C	39C	2DE	3139-66
Pulp type	O_2/alkali	O_2/alkali	ClO_2-alkali	kraft
Yield, % (kappa number)	72(100)	65(72)	71(65)	50(14)
	0.60 density			
Canadian freeness, ml	480	550	500	560
Zero-span breaking length, km	12.0	11.8	13.9	21.0
Burst factor	25	25	26	24
Breaking length, km	5.2	5.3	5.3	5.3
Tear factor (Elmendorf)	42	47	53	51
	0.70 density			
Canadian freeness, ml	180	255	150	410
Zero-span breaking length, km	13.9	12.8	14.8	21.2
Burst factor	38	39	55	55
Breaking length, km	7.1	7.0	8.4	8.9
Tear factor (Elmendorf)	41	43	57	78

At 0.60 sheet density, the strength properties were similar for the four pulps, although the holopulp had a somewhat higher tear factor. However, at 0.70 density, where three of the four pulps had low freenesses, the oxygen pulps did show definitely lower strength properties. Compensating for this lower

strength is the higher yield; pulp 19C represents 44% more pulp per ton of wood than the kraft, on a pulp basis.

Effect of Magnesium Ion on Strength Properties of High Consistency Pulps

As mentioned above magnesium ion has been shown by others to have a beneficial effect in oxygen/alkali pulping using sodium hydroxide (13). The beneficial effect was not observed in mildly alkaline solution (3a). It was of interest to evaluate its effectiveness in the present work. Table VII gives the properties of two pulps at the 72% yield level. One had 1% magnesium carbonate, and the other did not. The data show that kappa number, viscosity, and strength properties are virtually identical.

TABLE VII

COMPARISON OF HANDSHEET TEST DATA FOR 72% YIELD PULPS PREPARED WITH AND WITHOUT $MgCO_3$ ADDITION

Sample	19C		22C	
Additive	None		1% $MgCO_3$	
Pulp yield, % (kappa)	72(100)		72(102)	
Viscosity, cp	8.3		8.3	
PFI mill, counter rev's	100	400	100	400
Canadian freeness, ml	440	320	460	300
Handsheet density, g/cc	0.63	0.64	0.61	0.64
Zero-span breaking length, km	12.0	12.5	12.0	13.0
Burst factor	28	30	25	32
Breaking length, km	5.4	6.5	5.0	6.1
Tear factor (Elmendorf)	42	41	42	39

Table VIII gives a similar comparison at 65% yield. Again, the magnesium carbonate pulp was virtually the same as the control. This is consistent with the lack of an effect on yield and viscosity, mentioned earlier.

Comparison of High and Low Consistency Pulping on Pulp Properties

A limited number of runs was made at low consistency, in the reactor shown in Fig. 3. Table IX shows the sheet properties for pulps of 65-66% yield.

The kappa numbers and lignin contents were similar for the two pulps. The low consistency pulp was of higher brightness and viscosity, and took more refining to reach a comparable sheet density. The strength properties, particularly zero-span tensile strength, were better for the low consistency pulp.

TABLE VIII

COMPARISON OF 65-66% YIELD PULPS PREPARED WITH AND WITHOUT $MgCO_3$

Sample	39C		42C	
Additive	None		1% $MgCO_3$	
Yield (kappa)	65(72)		65(74)	
Viscosity, cp	6.7		6.5	
PFI mill, counter rev's	100	400	100	400
Canadian freeness, ml	400	200	400	210
Handsheet density, g/cc	0.65	0.72	0.67	0.71
Zero-span breaking length, km	12.5	13.0	12.0	13.0
Burst factor	32	42	33	40
Breaking length, km	6.3	7.2	6.4	7.1
Tear factor (Elmendorf)	47	45	43	43

TABLE IX

COMPARISON OF TEST DATA FOR 65-66% YIELD UNBLEACHED OXYGEN/ALKALI PULPS PRODUCED AT HIGH AND LOW CONSISTENCY

	Consistency			
	High		Low	
Sample	39C,42C		36	
Yield (kappa)	65(73)		66(77)	
TAPPI brightness	39		53	
Handsheet density, g/cc	0.66	0.72	0.66	0.72
PFI mill, counter rev's	100	400	400	700
Canadian freeness, ml	400	205	305	165
Zero-span breaking length, km	12.0	13.0	14.5	16.0
Burst factor	33	41	37	46
Breaking length, km	6.4	7.2	6.8	7.6
Tear factor (Elmendorf)	45	44	47	48

Several parameters were changed in addition to liquor-to-wood ratio in going from high to low consistency. The composition of the liquor, the cooking time, oxygen source (O_2 vs. air) and method of oxygen dissolution (i.e., spraying) are obvious differences. It is not known which of these is most important.

LOW CONSISTENCY PULPING OF RED MAPLE CHIPS

As mentioned previously, oxygen pulping has been plagued with the problem of making the oxygen available at the reaction site. Little success has been achieved using chips, and some work suggests that the maximum chip thickness which can be used is 2 mm (8). However, some success was obtained by others (14) on aspen chips using the same low consistency reactor and, therefore, a limited number of cooks was carried out on standard chips approximately 4 mm thick. It was hoped that the higher oxygen availability of the low consistency system, along with the higher total pressure, might help in making oxygen available at the reaction site.

Tables X and XI give the results for two different yield levels. At 65% yield, the handsheet produced from chips showed good formation, and the table shows that the strength properties were as good as or better than a 50% yield kraft, at the same sheet density. The low freeness, however, might be a problem. Unfortunately, no high-freeness samples were obtained on this run.

TABLE X

STRENGTH DATA FOR 65% YIELD OXYGEN PULP FROM CHIPS COMPARED WITH REFERENCE PULPS[a]

Sample	219	220	3139-66[b]
Type	O_2-chips	O_2-fiberized	kraft
Yield (kappa number)	65(75)	65(72)	50(14)
Freeness, ml	325	400	560
Zero-span breaking length, km	19.0	12.2	21.0
Burst factor	37	28	24
Breaking length, km	6.7	5.4	5.3
Tear factor (Elmendorf)	54	41	51

[a] Data interpolated for 0.60 density.

[b] Same data as in Table VII.

TABLE XI

STRENGTH DATA FOR OXYGEN PULPS FROM CHIPS AND FIBERIZED CHIPS[a]

Sample	218	215
Type	O_2-chips	O_2-fiberized
Yield (kappa number)	75(97)	76(97)
Freeness, ml	225	600
Zero-span breaking length, km	14.4	12.3
Burst factor	24	21
Breaking length, km	5.6	4.4
Tear factor	54	53

[a]Data extrapolated to 0.50 sheet density.

At 75% yield, the handsheets from chips showed definite shives, and the strength data may not be as good on such coarse pulp. Also, the data were extrapolated, as there was no overlap in the sheet density for the two series. This may be due to a problem in the sheet density determination in the presence of shives. Nevertheless, the properties of the sample from chips compare favorably to those from fiberized chips. This area deserves further exploration particularly as no screening or cleaning has been employed on these pulps.

EVALUATION OF STRENGTH LOSS VS. YIELD INCREASE

Like most new processes, oxygen/alkali pulping offers some advantages and some disadvantages over present technology (kraft). The advantages (higher yield, no need for odor control, possibly simplified chemical recovery) are obtained only at the price of lower strength and less fuel value in spent liquor. Since most hardwood pulps tend to be used for nonstrength purposes (e.g., printing papers), this may not be of great concern. Nevertheless, it is useful to consider how the strength loss is compensated for by higher yield.

One method of comparison is to consider the strength on a wood basis instead of a pulp basis. By multiplying strength by yield (fraction, not percent), strength-yield factors can be obtained, and these are given in Table XII. Another way of looking at it is that in order to make paper of a given strength, weaker pulps must require higher basis weights. Assuming strength to be proportional to basis weight, the numbers in the table are proportional to the area of such paper that can be made from a unit of wood by the various processes. No attempt was made to take the other factors above into account.

TABLE XII

STRENGTH-YIELD FACTORS[a] FOR KRAFT AND HIGH-YIELD OXIDATIVE PULPS[b]

Sample	19C	39C	2DE	3139-66
Pulp type	O_2/alkali	O_2/alkali	ClO_2-alkali	kraft
Yield, %	72	65	71	50
	0.60 density			
Zero-span factor	8.6	7.7	9.9	12.0
Burst factor factor	18	16	19	12
Breaking length factor	3.7	3.5	3.8	2.7
Tear factor factor	30	31	38	26
	0.70 density			
Zero-span factor	10.0	8.3	10.5	10.6
Burst factor factor	27	25	39	28
Breaking length factor	5.1	4.6	6.0	4.5
Tear factor factor	29	28	40	39

[a] Factor = strength property x yield/100.

[b] Data from Table VII.

The data at 0.60 density suggest an advantage for the high-yield pulps. With the exception of zero-span, the factors are generally higher for the oxygen and holopulps than for the kraft. At 0.70 sheet density, the holopulp looks best and the factor for tear looks lowest for the oxygen pulps.

This comparison represents one term in the overall equation which must be solved in order to determine the practicality of oxygen pulping. In hardwood

pulps, where strength may not be the primary concern, it may be a relatively small term. In softwood pulps, where strength is a major objective, the analogous comparison could be more important.

BLEACHING OF OXYGEN PULPS

The ideal combination would be a nonsulfur pulping process combined with a nonchlorine bleaching process. This would solve both odor and corrosion problems and, hopefully, lead to lower chemical cost. However, the state of the art has not reached that point for chemical pulps. In the present study, the objective at this point was to demonstrate the bleachability of the oxygen pulps produced, with a target brightness of 85. Of special interest was the affect on yield.

Two high-consistency oxygen pulps were prepared for bleaching, and two control pulps were bleached for comparison. The oxygen pulps were at higher kappa numbers than the controls. Viscosity and optical data are given in Table XIII. The bleaching conditions are given in the Experimental section. As can be seen in the table, a larger yield loss was observed in bleaching the three high-yield oxidative pulps, compared to kraft and, thus, a portion of the yield advantage is lost. However, no difficulty was encountered in reaching the target brightness. Brightness reversion upon steam aging was similar for all pulps.

The strength properties for these pulps are given in Table XIV at comparable sheet densities. It can be seen that the strength values for the oxygen pulps are almost as good as those of kraft. This demonstrates that an acceptable bleached pulp based on oxygen pulping can be prepared at high yield with properties approaching those of kraft. Note that the higher yield and viscosity obtained with potassium iodide in pulping was maintained after bleaching.

TABLE XIII

VISCOSITY AND OPTICAL DATA ON OXYGEN/ALKALI AND OTHER BLEACHED PULPS

	Inhibitor		Control	
	$MgCO_3$	KI	ClO_2-Alkali	Kraft
Sample	BL65C	BL69C	BL2DE	BL3139-66
Yield, % unbleached	64	66	∿66	50
Yield, % bleached	54	58	∿58	47
Kappa number (unbleached)	66	51	25	14
Viscosity, cp, unbleached	7.2	15.6	n.a.	n.a.
Viscosity, cp, bleached	6.3	15.3	n.a.	n.a.
Bleached brightness	85	88	∿86	∿89
Steam-aged brightness[a]	77	83	∿78	∿81
Spec. scattering coeff., 650 nm	317	313	245	425
Spec. abs. coeff., 650 nm	0.72	0.59	1.04	0.85

[a] Gullichsen, J., Paperi Puu 47(4a):215(1965).

TABLE XIV

COMPARISON AT SIMILAR DENSITIES OF STRENGTH DATA FOR HIGH-YIELD OXYGEN/ALKALI PULPS WITH BLEACHED KRAFT PULP

Sample	BL65C		BL69C		BL3139-66	
Pulp type	O_2-alkali		O_2-alkali		kraft	
Yield, % bleached	54		58		47	
Inhibitor	$MgCO_3$		KI		n.a.	
Sheet density, g/cc	0.71	0.76	0.71	0.75	0.70	0.75
PFI mill, counter rev's	0	50	0	50	400	800
Canadian freeness, ml	475	380	475	370	410	315
Zero-span breaking length, km	15.0	15.0	17.5	18.0	19.7	20.2
Tear factor (Elmendorf)	57	56	65	67	70	79
Burst factor	50	55	46	55	44	56
Breaking length, km	6.8	8.0	6.8	8.4	7.2	8.1

RELATIONSHIP BETWEEN VISCOSITY AND ZERO-SPAN TENSILE STRENGTH

Pulp viscosity is generally a useful measure of the papermaking potential of a pulp. Since it is related to a fundamental chemical property of the carbohydrates (molecular weight), it should be independent of beating and other process steps which precede strength tests. Therefore, viscosities were measured for a

number of samples, but it soon became obvious that the low values obtained did not reflect the strength properties ultimately measured on handsheets.

In theory, zero-span tensile strength measures the strength of fibers, as opposed to bonding strength. As such, these measurements are also relatively insensitive to the sample preparation. It was, therefore, of interest to consider whether there was a correlation between zero-span tensile strength and viscosity. Table XV and Fig. 6 give the results. Linear regression analysis showed a very poor correlation ($\underline{r}^2 = 0.08$) between these two variables. There was also very little correlation between viscosity and yield ($\underline{r}^2 = 0.03$), but there was a significant correlation between zero-span and yield ($\underline{r}^2 = 0.72$), which would be expected on the basis of the number of fibers per gram.

TABLE XV

PULP VISCOSITIES AND ZERO-SPAN TENSILE STRENGTHS

Sample	Yield	Viscosity	Zero-span Tensile[a]	Corrected Zero-span[c]
36	66.4	9.9	13.2	13.5
39C	65.5	6.5	12.2	12.3
42C	65.1	6.7	12.3	12.3
65C	64.1	7.2	13.7	13.5
7C	71.9	6.0	10.0[b]	11.1
11C	80.2	11.2	11.0[b]	13.6
12C	78.8	8.9	10.9[b]	13.2
19C	72.3	8.3	12.1	13.5
22C	72.2	8.3	12.0	13.3
118C	63.5	6.7	12.7	12.4
BL65B	54.3	6.3	16.1	13.4
BL69C	58.2	15.3	18.5	16.6
BL115C	54.5	6.8	15.7	13.2
BL128C	56.3	6.6	17.2	14.9

[a] Measured after 100 PFI mill counter rev's unless otherwise noted.

[b] Measured after 50 PFI counter rev's.

[c] Corrected to 65% yield by multiplying by yield and dividing by 65.

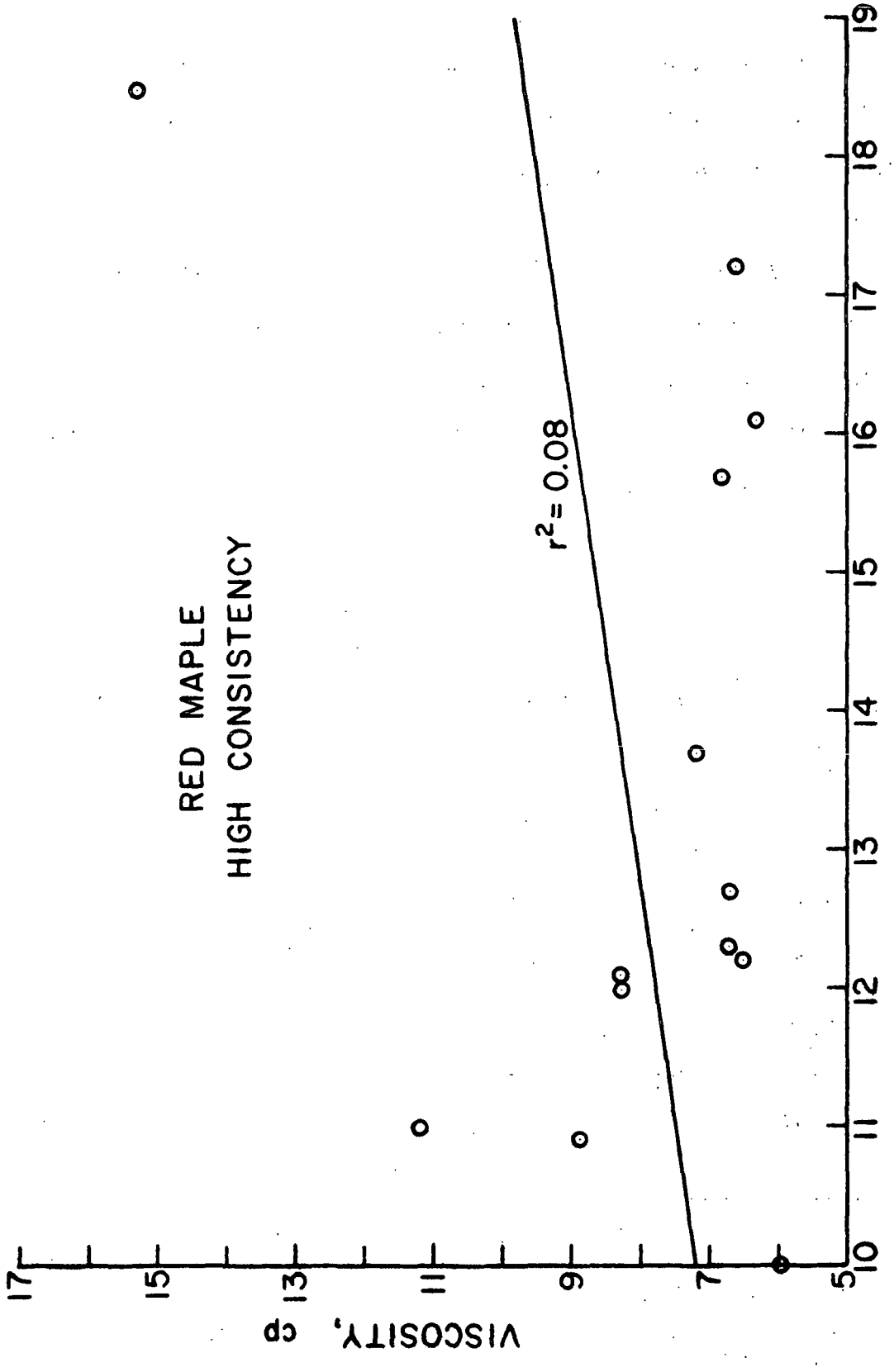

Figure 6. Viscosity vs. Zero-span for Selected Red Maple Pulps

When the zero-span data are corrected to the same number of fibers, much of the correlation between zero-span and yield is removed ($r^2 = 0.11$), and the correlation between zero span and viscosity becomes greater ($r^2 = 0.56$). Nevertheless, the correlation is not strong enough to use only one of these measurements in evaluating the pulps.

An improved method of molecular weight estimation is being developed under IPC Project 3284. A report will soon be issued containing details of the new method.

CORRELATION BETWEEN KAPPA NUMBER AND KLASON LIGNIN

The problem of determining the lignin content of oxygen pulps has been discussed in another report (15) in relation to lignin activation. In the present context, it was of interest to consider the relationship between kappa number and Klason lignin. Thirty-seven pulps were analyzed for Klason lignin and acid-soluble lignin (16). Yields ranged from 65 to 85%. The data are given in the Appendix, while Fig. 7 shows total lignin vs. kappa number. The values were analyzed by linear regression and the following equations were obtained:

$$\text{Klason lignin} = -2.55 + 0.152 \text{ kappa} \quad (r^2 = 0.94)$$

$$\text{Klason + acid-soluble lignin} = 1.54 + 0.160 \text{ kappa} \quad (r^2 = 0.94)$$

The two equations have essentially the same slope and the difference in intercept reflects a relatively constant acid-soluble lignin content, although one might expect a zero intercept for the second equation. The slope is remarkably similar to the value of 0.15 observed typically in kraft pulps (18). A linear relationship has also been reported between kappa number and lignin content by Wollwage, et al. (18), who was working with southern pine, and Landucci and Sanyer (3a) suggest a slope of 0.17 for loblolly pine oxygen pulps.

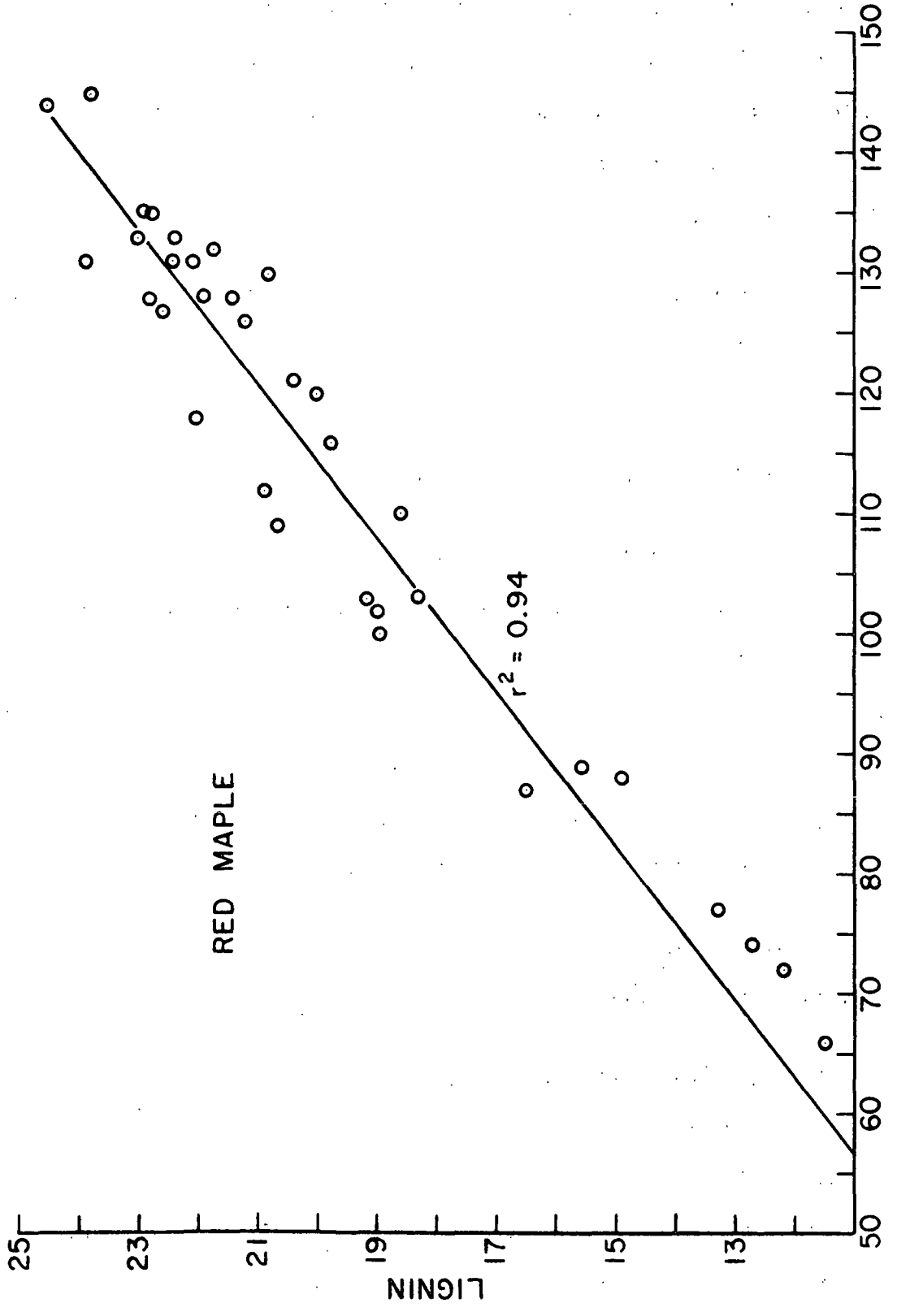

Figure 7. Total Lignin vs. Kappa Number

FUTURE WORK

The emphasis on this project will shift to softwoods. Loblolly pine will be used as a typical softwood. Both high and low consistency pulping will be studied. Some effort will be made to characterize and minimize the mechanical damage during fiberization. The goal of high yields will be maintained, although it is expected that yields somewhat lower than those observed for maple will be encountered.

A new project has been started (Project 3342) which will use computer simulation to look into the economics of various configurations for pulping. It is hoped that it will provide some guidance on optimum sequences and conditions for oxygen and other pulping processes.

EXPERIMENTAL

GENERAL

Kappa numbers and Klason lignin were determined by the standard procedures (17,19). Acid-soluble lignin was determined by the method of Pearl and Busche (16) and involved the measurement of the absorbance at 208 nm of the supernate in the Klason lignin determination. Cuene viscosities were determined by the standard procedure (20) after delignification with acid chlorite at room temperature for 24 hours. Pulp strength tests were carried out by standard methods.

FIBERIZATION

Fiberization was done on pilot-plant equipment under 80 psig steam pressure (160°C) at moisture contents of 57-60% and plate settings of approximately 0.030 inch. Samples which were fiberized in the presence of alkali were impregnated at approximately 10% consistency for 30 minutes at 93° with sodium carbonate (4.9% retained as Na_2O) and the excess liquor removed before fiberization.

HIGH-CONSISTENCY DELIGNIFICATION

Oxygen/sodium carbonate cooks were carried out in a 2000-ml Parr stainless steel bomb equipped with a Teflon liner. Fiber samples were soaked for 30 minutes with the alkali and excess solution was removed by filtration to give the desired consistency (28-29%). The fiber sample (120 g o.d. fiber) was placed in the preheated bomb, which was then immersed in an oil bath, often at a temperature somewhat lower than the temperature for the cook. The sample was brought quickly up to the bath temperature by introduction of steam, and then the oxygen was applied. The time-temperature cycle was produced by changing the temperature of the oil bath. In some cases, pulps were cooked in two stages, with a water wash in between. Specific conditions are given in Table XVI.

TABLE XVI

OXYGEN/ALKALI COOKING CONDITIONS

Cook	Total Alkali, as Na_2O, %	Temp., °C	Time to Temp., min	Time at Temp., min	Pressure[a]
		High Consistency			
11C	5.6	120	100	140	130
19C,22C	9.4[b]	120	100	140	130
30B,39B,39C, 40B,42C,62B, 65B,65C,66B, 67B,68B,69B, 69C,118C	10.5[b]	120	100	320	130
81	5.2	120	40	120	130
85	5.3	130	40	60	130
87	5.1	120	40	240	130
93	5.0	130	40	240	130
95	5.3	120	40	240	60
96	5.2	130	40	60	300
99	5.1	120	40	120	60
100	5.3	130	40	240	60
104	5.4	120	40	120	300
106	5.3	130	40	60	60
107	5.0	120	40	240	300
		Low Consistency			
35,37,38	65	120	10	160	550
36	65	120	10	210	550
130,131,132,133	65	130	10	90	540
215	65	120	10	160	480
218	32	130	10	220	470
219	32	130	10	340	470
220	65	120	10	250	480

[a] Partial pressure of oxygen, measured or calculated for 100°C.

[b] Cooks in these groups were cooked twice under these conditions, using half the alkali for each cook.

LOW-CONSISTENCY DELIGNIFICATION

Low-consistency runs were carried out in equipment built by Zimpro, Inc. The equipment was designed for high-pressure air. Samples (ca. 200 g) were fluffed into a stainless steel mesh basket which was then lowered into the reactor which contained 15 liters of liquor containing 9.9 g/liter of sodium carbonate and 7.6 g/liter of sodium bicarbonate. This mixture was chosen to simulate the recovered liquor from a wet-combustion recovery system, and it also provides a low pH, which helps prevent carbohydrate degradation. The reactor was heated rapidly (ca. 10 minutes) with steam while the circulating liquor was brought up to temperature with a heat exchanger. Air pressure (2950 or 2600 psig, or 520-590 psi oxygen partial pressure) was applied during the heatup and was maintained with a compressor and slow bleed. At the end of a run, the temperature was rapidly reduced by water-cooling the reactor and cooling the circulating liquor in the heat exchanger. The high liquor-to-wood ratio could probably be reduced by increasing the size of the wood sample and changing the configuration of the reactor. Specific conditions are given in Table XVI.

KRAFT COOKING CONDITIONS

Kraft pulp 3139-66 was prepared as follows:

Liquor:wood ratio	4
Active alkali, as Na_2O, %	15
Sulfidity, %	28
Temperature, °C	180
Time to temperature, min	90
Time at temperature, min	60

PREPARATION OF HOLOPULP

Holopulp 2DE was prepared in a DED sequence as follows:

Stage I: 4% ClO_2 (as ClO_2), 12% consistency, 45 min at 25-35°C

Stage II: 7% NaOH (as NaOH), 15% consistency, 120 min at 80°C

Stage III: 4% ClO_2, 12% consistency, 45 min at 25-30°C

BLEACHING STUDIES

The kraft pulp was bleached under conditions shown in Table XVII, while the oxygen/alkali pulps were bleached as given in Table XVIII.

TABLE XVII

BLEACHING CONDITIONS FOR KRAFT PULP

	Bleaching Stage			
	I	II	III	IV
Consistency, %	3.0	10	10	10
Temperature, °C	25	65	35	70
Chlorine, %	2.5	--	--	--
Sodium hydroxide, %	--	1.7	--	--
Sodium hypochlorite (as avail. Cl_2), %	--	--	0.5	--
Chlorine dioxide	--	--	--	0.6
Time, min	45	90	105	240
Final pH	2.2	11.3	8.3	3.2

TABLE XVIII

BLEACHING OXYGEN/ALKALI PULPS

	Bleaching Stage			
	I	II	III	IV
Consistency, %	10	10	10	10
Temperature, °C	70	70	70	70
Chlorine dioxide, %	2.0	--	1.0	--
Sodium hydroxide, %	--	2.5	--	≥0.13
Peroxide, %	--	--	--	1.0[a]
Time, min	20	90	35-55	180
Final pH	3.5	10.8	3.8	8.2-9.6

[a]Peroxide included $MgSO_4$ and 5% silicate (peroxide basis); additional 3.0% silicate (on pulp) added for pulp 69C.

ACKNOWLEDGMENTS

Most of the experimental work described in this report was carried out by V. J. Van Drunen, H. M. Corbett and L. B. Edminster. Evaluation data were obtained by the Analytical Department and the Paper Evaluation Laboratory. The expert and willing assistance of these people is gratefully acknowledged. The cooperation of Clarence Hoffman and Zimpro, Inc. is also to be acknowledged. In addition, the project leadership of G. A. Nicholls through the major portion of this work is recognized.

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APPENDIX

MULTIPLE LINEAR REGRESSION ANALYSIS OF PULPING VARIABLES

Regression analyses were carried out on 64 high-consistency cooks. These cooks constituted early runs (Sample numbers 2-73, 112-118, 125) which generally involved long reaction times, including multiple cooks. In addition, the pulping variables were not changed in a systematic fashion and, therefore, there is some correlation between variables. More recent work, in which these variables were changed more systematically, is discussed in part in the section "Effect of Pulping Variables on Yield at High Consistency." However, the yield levels in that section are generally quite high ($\geq$ 75%). Since the cooking cycle was different in those more recent results, they were not included in this statistical analysis, but will be considered separately at a later date when more complete data are available.

The following two equations were obtained from the regression analysis:

$$\begin{aligned}\text{Yield} = 94.74 &- (0.926 \pm 0.053)\ Na_2O + (0.0209 \pm 0.0056)\ \text{Time} \\ &- (0.00989 \pm 0.00330)\ \text{Pressure} - (0.0472 \pm 0.0426)\ \text{Temperature} \\ &- (0.0106 \pm 0.0014)\ (\text{Time})\ (\text{Temperature Parameter}) \qquad (1)\end{aligned}$$

$$\begin{aligned}\text{Yield} = 76.95 &- (1.34 \pm 0.06)\ Na_2O + (0.443 \pm 0.042)\ \text{Time} \\ &- (0.0125 \pm 0.0026)\ \text{Pressure} + (0.118 \pm 0.044)\ \text{Temperature} \\ &- (0.00384 \pm 0.00035)\ (\text{Time})\ (\text{Temperature}) \qquad (2)\end{aligned}$$

In these equations, sodium carbonate is expressed as percent Na_2O on an o.d. wood basis; time, temperature, and pressure are in minutes, degrees centrigrade, and oxygen pressure equivalent at 100°, respectively. A Temperature Parameter was used in place of temperature in the interaction term in Equation (1). It is

based on the assumption that the reaction rate doubles for each 10° rise in temperature. It was set equal to 1.0 for 100°, 4.0 for 120°, and 8.0 for 130°.

The first equation (r^2 = 0.97) predicts that increasing alkali or pressure will lower yield, since there is a negative coefficient associated with these terms. Two terms must be considered to assess the effect of changing temperature or time. Since both terms are negative in the case of temperature, an increase is predicted to lower yield. The two coefficients for time have opposite signs, so the prediction is that increased time will only lower yield at temperatures higher than 110°. This low-temperature prediction is unreasonable and is probably caused by the small number of samples at temperatures lower than 120°.

The second equation (r^2 = 0.98) predicts that increased alkali and pressure would tend to lower the yield; increased time would lower the yield only for temperatures greater than 115° [similar to Equation (1)] and increased temperature would lower the yield only for times greater than 30 minutes (which was the case in all but six of the samples).

These equations, which might be refined in future work, are useful in predicting the yields over the rather limited ranges of the variables considered here. Their predictive power for the more recent runs is limited to longer reaction times, where the different cooking cycle would have a smaller effect.

DATA USED FOR REGRESSION OF ANALYSIS OF KAPPA NUMBER VS. LIGNIN CONTENT

Table XIX gives the data which were used in the regression analysis discussed in the text.

TABLE XIX

SUMMARY OF LIGNIN ANALYSES AND KAPPA NUMBERS

Sample No.	Yield, %	Kappa No.	Klason Lignin, %	Acid Soluble Lignin, %
7C	71.9	132	15.4	6.3
11C	80.2	128	17.0	5.8
12C	78.8	145	17.8	6.0
19C	72.3	100	13.2	5.8
22C	72.2	102	13.7	5.3
5A	81.1	127	16.8	5.8
13B	68.0	87	11.4	5.1
15A	76.4	109	15.2	5.5
17B	75.5	103	14.1	5.1
24A	80.4	118	17.4	5.6
25A	80.9	135	17.4	5.4
26A	82.2	132	18.5	5.4
27A	83.8	139	19.1	5.4
28	76.9	121	16.0	4.4
29	79.0	112	16.2	4.7
31	81.5	128	16.8	4.6
32	84.1	131	17.8	4.6
33	85.1	133	18.6	4.4
49	78.4	130	15.9	4.9
50	80.7	133	17.4	5.0
51	75.3	110	14.0	4.6
52	77.6	116	15.0	4.8
54	80.8	131	17.0	5.1
55	81.1	135	18.0	4.9
56	77.6	120	15.1	4.9
58	82.1	135	18.0	4.8
57	80.5	126	16.2	5.0
59	76.3	103	13.3	5.0
60	81.9	128	16.9	5.0
61	75.9	120	14.8	5.2
35/38C	69.7	89	10.0	5.6
36	66.4	77	7.8	5.5
37	68.7	88	9.2	5.7
39C	65.5	74	8.5	4.2
42C	65.1	72	8.0	4.2
65C	64.1	66	7.4	4.1
69C	66.0	51	5.4	4.0